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GAS-PHASE OXIDATION OF ALUMINUM ATOMS

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9

Table of Contents

A. Accomplishments During this Grant Period

We have published two articles pertaining to the gas-phase oxidation of metals, one on the detection of metal oxide products by the new technique of laser-induced fluorescence, the other on the chemiluminescent reaction $A\ell + O_3 \rightarrow A\ell O^* + O_2$ from which we have determined the energy of the aluminum monoxide bond. A brief synopsis of each paper follows:

A. Schultz, H. W. Cruse, and R. N. Zare, "Laser-Induced Fluorescence: A Method to Measure the Internal State Distribution of Reaction Products," J. Chem. Phys. 57, 1354 (1972).

In a molecular beam apparatus, a thermal beam of barium atoms ($T \approx 1100°K$) intersects an uncollimated, thermal beam of O_2 molecules ($T \approx 300°K$) and reacts to form $BaO(X\ ^1\Sigma) + O(^3P) + 0.66$ eV. Simultaneously, light from a pulsed (2 - 10 nsec duration), tunable dye laser passes through the reaction zone. As the wavelength of the dye laser is scanned, the BaO molecules are excited to the (v', J') level whenever the laser wavelength coincides with an allowed v"J" → v'J' transition in the

A - X band system. The resulting fluorescence emitted at right angles to the laser beam is detected by a fast-response photomultiplier. The laser pulse triggers a boxcar integrator .(Princeton Applied Research or Keithley Instruments) whose electronic gate (window) is maintained open from the time of the laser pulse to 2 - 5 times the· BaO A state lifetime. This analog device permits us to average the signals resulting from many laser pulses. The scattered light from the laser beam is rejected either with a sharp cutoff Corning filter or by delaying by typically 20 nsec the opening of the electronic gate.

The BaO fluorescence rate versus laser wavelength gives the vibrational structure in a fast scan and shows the partially resolved rotational structure in a slow scan. Preliminary analysis of the data yields the population ratios $N_0 : N_1 : N_2 : N_3 : N_4 : N_5 : N_6 : N_7 = 1.00 : 0.53 : 0.37 : 0.30 : 0.20 : 0.13 : 0.11 : 0.10$, which fits moderately well a Boltzmann distribution of $2500°K$. The average vibrational energy is approximately 0.25 eV, about one-third of the total energy available (reaction exothermicity plus initial kinetic energies of the

reactants).

We are also able to measure directly the BaO A state radiative lifetime. Using a swept narrow sampling window, our first lifetime measurements for $v' \geq 3$ give a value of 350 ± 50 nsec, in reasonable agreement with Johnson.[1]

J. L. Gole and R. N. Zare, "Determination of D_0^0(AlO) from Crossed-Beam Chemiluminescence of $Al + O_3$," J. Chem. Phys. 57, 5331 (1972).

In a molecular beam apparatus, a thermal beam of aluminum atoms ($\approx 1700^\circ$K) intersects an uncollimated thermal beam of ozone molecules (300°K) and the resulting visible chemiluminescence is recorded with a 1 m scanning monochromator. The chemiluminescence spectrum consists of (1) the AlO B $^2\Sigma^+$ - X $^2\Sigma^+$ blue-green system for which we have assigned bands to the strongly structured features in the region 4200 - 4900 Å, and (2) more intense weakly structured features in the region 4500 - 8500 Å, which appear to be emission from a polyatomic aluminum oxide on which there seems to be superimposed the AlO B $^2\Sigma^+$ - A $^2\Pi$ band system. From the

chemiluminescent spectrum a minimum value of 5.13±0.05 eV
is deduced for the dissociation energy of the ground
state of aluminum oxide. By accepting the upper limit
of 5.20 eV deduced by MacDonald and Innes from Tyte's
shock tube absorption data, we recommend the value
$D_0^0(A\ell O) = 5.15\pm0.5$ eV.

In brief, the chief signficance of the paper by Schultz
et al. is that the feasibility of using laser-induced fluores-
cence as a new molecular beam detector is established. It will
be possible to determine the relative vibrational (and rotational)
population distribution of $A\ell O$ formed in the reaction $A\ell + O_2 \rightarrow$
$A\ell O + O$. The chief significance of the paper by Gole et al. is
that the reaction $A\ell + O_2 \rightarrow A\ell O + O$ is nearly thermoneutral so that
only the lowest vibrational levels of $A\ell O$ are expected to be
appreciably populated.

B. Work in Progress

a) High-Temperature Oven

During this period we have designed an oven source for generating beams of aluminum atoms. It is necessary to heat aluminum to 1750°K in order to obtain a vapor pressure of one torr. The oven has been designed to reach a maximum operating temperature of 1900°K. The heating element is a molybdenum tube (0.015 inches wall thickness) through which current (300 - 600 Amps) is passed. The heating element is surrounded by several heat shields. Inside the cylindrical heating element is a molybdenum container (N.B. we have found that tantalum is attacked by molten aluminum worse than molybdenum). The aluminum, itself, is placed in a boron nitride crucible inside the Mo container. This is necessary because molten aluminum creeps on a molybdenum surface.[2] This type of oven design has been used sucessfully to produce beams of $BaCl_2$ with an operating temperature of 2200°K.[3]

b) Oven Vacuum Chamber

In addition to the oven, a new vacuum chamber is to be constructed to house the oven. This chamber will be mated to

the present apparatus in which the earlier $Ba + O_2 \rightarrow BaO + O$ laser-induced fluorescence studies were carried out (see above).

c) Secondary Beam Source

The above two items await fabrication by our machine shop. During this period we have also designed, constructed, and successfully tested a liquid-nitrogen pumped secondary beam source. For gases that are condensable at $77^\circ K$, such as O_3, NO_2 and N_2O, this modification permits us to study gas-phase chemical reactions using _two_ crossed beams, rather than the previous work in which a metal beam passes through a tenuous atmosphere of reactant gas.

d) Immediate Future Plans

Upon completion of the oven and its housing, we intend to produce a beam of aluminum atoms, whose flux will be measured using a Granville-Phillips film thickness moitor. We then plan to introduce a small controlled leak of O_2 into the reaction chamber and search for the production of $A\ell O$ using the laser-induced fluorescence technique.

References

1. S. E. Johnson, J. Chem. Phys. <u>55</u>, 149 (1972).

2. H. Lew, Phys. Rev. <u>76</u>, 1086 (1949).

3. P. J. Dagdigian and L. Wharton, "Stark Effect of $BaCl_2$," J. Chem. Phys. (accepted for publication).